

CLAIMS

What is claimed is:

5 1. A polyurethane sealant comprising the reaction product of:

- a) a hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component;
- b) an isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component; and

10 c) at least one of:

- i) a diphenylmethane diisocyanate prepolymer component; or
- ii) a diphenylmethane diisocyanate monomer component;

wherein said polyurethane sealant is paintable in the absence of a primer and has a 100% modulus of less than about 100 psi in the absence of a plasticizer, and wherein diphenylmethane diisocyanate (calculated as monomer) is about 1% to about 3% by weight of said reaction product.

15 2. The polyurethane sealant of claim 1, wherein the at least one of a diphenylmethane diisocyanate prepolymer component and a diphenylmethane diisocyanate monomer component is provided as a mixture with at least one of a hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component or an isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component.

20 25 3. The polyurethane sealant of claim 1, wherein the polyoxyalkylene polyol of the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component is selected from the group consisting of polyethylene ether glycol, polypropylene ether glycol, poly(tetramethylene ether) glycol, polyethers prepared by

the copolymerization of cyclic ethers selected from the group consisting of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, and mixtures thereof, with aliphatic polyols selected from the group consisting of ethylene glycol, 1,3-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and mixtures thereof, and combinations thereof.

- 5 4. The polyurethane sealant of claim 1, wherein the polyoxyalkylene polyol of the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component is selected from the group consisting of polyethylene ether glycol, polypropylene ether glycol, poly(tetramethylene ether) glycol, polyethers prepared by the copolymerization of cyclic ethers selected from the group consisting of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, and mixtures thereof, with aliphatic polyols selected from the group consisting of ethylene glycol, 1,3-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and mixtures thereof, and combinations thereof.
- 10 5. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate prepolymer component additionally comprises an allophanate.
- 15 6. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate prepolymer component additionally comprises a polyoxyalkylene polyol.
- 20 7. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate prepolymer component is isocyanate-terminated.
- 25 8. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate prepolymer component is hydroxy-terminated.
9. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate (calculated as monomer) is about 1% to about 2% by weight of the reaction product.
10. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate (calculated as monomer) is about 2% to about 3% by weight of the reaction product.

11. The polyurethane sealant of claim 1, wherein the toluenediisocyanate (calculated as monomer) is about 1% to about 20% by weight of the reaction product.
12. The polyurethane sealant of claim 1, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component has a number 5 average molecular weight in the range of about 3,000 to about 20,000.
13. The polyurethane sealant of claim 1, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component has a number average molecular weight in the range of about 6,000 to about 15,000.
14. The polyurethane sealant of claim 1, wherein the isocyanate-terminated 10 toluenediisocyanate/polyoxyalkylene polyol activator component has a number average molecular weight in the range of about 1,000 to about 4,000.
15. The polyurethane sealant of claim 1, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component has a number average molecular weight in the range of about 1,500 to about 3,500.
16. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate component has a number average molecular weight in the range of about 250 to about 4,000.
17. The polyurethane sealant of claim 1, wherein the diphenylmethane diisocyanate component has a number average molecular weight in the range of about 20 250 to about 2,000.
18. The polyurethane sealant of claim 1, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component comprises about 10% to about 92% by weight of the reaction product.
19. The polyurethane sealant of claim 1, wherein the hydroxy-terminated 25 toluenediisocyanate/polyoxyalkylene polyol prepolymer component comprises about 20% to about 80% by weight of the reaction product.

20. The polyurethane sealant of claim 1, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component comprises about 1% to about 40% by weight of the reaction product.
21. The polyurethane sealant of claim 1, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component comprises about 5% to about 20% by weight of the reaction product.
22. The polyurethane sealant of claim 1, wherein the sealant has a 100% modulus of about 40 psi to about 90 psi.
23. The polyurethane sealant of claim 1, wherein the sealant has a tensile strength of about 100 psi or greater.
24. The polyurethane sealant of claim 1, wherein the sealant has an elongation to break of about 200% or greater.
25. The polyurethane sealant of claim 1, wherein the mole ratio of isocyanate-terminated end groups to hydroxy-terminated end groups is about 0.5:1 to about 3:1.
26. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one component selected from the group consisting of UV absorbers, antioxidants, stabilizers, mildewcides, biocides, fungicides, fire or flame retardants, fillers, pigments, adhesion promoters, flow and leveling additives, wetting agents, antifoaming agents, rheology modifiers, and mixtures thereof.
27. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one UV stabilizer selected from the group consisting of 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, esters of substituted and unsubstituted benzoic acids, acrylates, nickel compounds, sterically hindered amines, oxanilides, 2-(2-hydroxyphenyl)-1,3,5-triazines, and mixtures thereof.
28. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one antioxidant selected from the group consisting of alkylated monophenols, alkylthiomethylphenols, hydroquinones and alkylated hydroquinones, tocopherols, hydroxylated thiadiphenyl ethers, alkylidenebisphenols, O-, N- and S-benzyl compounds, hydroxybenzylated malonates, aromatic hydroxybenzyl

compounds, triazine compounds, benzylphosphonates, acylaminophenols, esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, esters of beta-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, amides of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, ascorbic acid and derivatives, aminic antioxidants, and mixtures thereof.

29. The polyurethane sealant of claim 1, wherein the reaction product additionally 10 comprises at least one fire or flame retardant selected from the group consisting of triphenyl phosphate, polyammonium phosphate, monoammonium phosphate, tri(2-chloroethyl) phosphate, melamine, exfoliated graphite, acid treated natural graphite flakes, and mixtures thereof.

30. The polyurethane sealant of claim 1, wherein the reaction product additionally 15 comprises at least one filler selected from the group consisting of carbon black, titanium dioxide, zinc oxide, glass spheres, iron particles, quartz, hydrophilic silica, hydrophobic amorphous fumed silica, amorphous precipitated silica, barytes, limestone, sulfates, alumina, clays, diatomaceous earth, wollastonite, mica, perlite, flint powder, kryolite, talc, polymer granules, polymer powders, micronized 20 polymers, melamine, zinc oxide, and mixtures thereof.

31. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one pigment selected from the group consisting of carbon black, titanium dioxide, barium sulfate, zinc oxide, zinc sulfide, basic lead carbonate, 25 antimony trioxide, lithopones, iron oxides, graphite, luminescent pigments, zinc yellow, zinc green, ultramarine, manganese black, antimony black, manganese violet, Paris blue, Schweinfurter green, sepia, gamboge, Cassel brown, toluidine red, para red, Hansa yellow, indigo, azo dyes, anthraquinonoid and indigoid dyes, dioxazine, quinacridone, phthalocyanine, isoindolinone, and metal complex pigments, and mixtures thereof.

30 32. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one flow and leveling additive, wetting agent, or antifoaming agent

selected from the group consisting of silicones, modified silicones, hydrocarbons, polyacrylates, fluorosurfactants, and mixtures thereof.

33. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one rheology modifier selected from the group consisting of fumed 5 silica, hydroxyethyl cellulose, hydroxypropyl cellulose, polyamide waxes, modified castor oil, clay intercalated with organic cations and mixtures thereof.

34. The polyurethane sealant of claim 1, wherein the reaction product additionally comprises at least one adhesion promoter selected from the group consisting of 10 2-aminoethyl-dimethylmethoxysilane; 6-aminoethyl-tributoxysilane; 3-aminopropyl-trimethoxysilane; 3-aminopropyl-triethoxysilane; 3-aminopropyl-methyldiethoxysilane; 5-aminopentyl-trimethoxysilane; 5-aminopentyl-triethoxysilane and 3-aminopropyl-triisopropoxysilane, γ -glycidoxypolytrimethoxysilane, γ -glycidoxypolytriethoxysilane, 15 γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, and, γ -ureidopropyltrimethoxysilane, and γ -ureidopropyltriethoxysilane.

35. The polyurethane sealant of claim 1, wherein at least one reaction product component additionally comprises at least one chain extender selected from the group 20 consisting of hydroxyl containing chain extenders and amine containing chain extenders.

36. The polyurethane sealant of claim 35, wherein said chain extender is selected from the group consisting of ethylene glycol, 1,3-propanediol, 2-methyl-1,3- 25 propanediol, 1,4-butanediol, neopentyl glycol, diethylene glycol, ethylene diamine, 1,3-propanediamine, 1,4-butanediamine, 1,3-pentanediamine, 1,5-pentanediamine, 1,6-hexamethylene diamine, 2-methylpentamethylenediamine, and mixtures thereof.

37. A multicomponent formulation comprising:

- a) a hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component;
- b) an isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component; and
- c) at least one of:
 - i) a diphenylmethane diisocyanate prepolymer component; or
 - ii) a diphenylmethane diisocyanate monomer component;

10 wherein when components a, b, and c are combined, a polyurethane reaction product is formed that is paintable in the absence of a primer and has a 100% modulus of less than about 100 psi in the absence of a plasticizer, and wherein diphenylmethane diisocyanate (calculated as monomer) is about 1% to 3% by weight of said reaction product.

15 38. The multicomponent formulation of claim 37, wherein the at least one of a diphenylmethane diisocyanate prepolymer component or a diphenylmethane diisocyanate monomer component is provided as a mixture with a hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component.

20 39. The multicomponent formulation of claim 37, wherein the at least one of a diphenylmethane diisocyanate prepolymer component or a diphenylmethane diisocyanate monomer component is provided as a mixture with an isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component.

25 40. The multicomponent formulation of claim 37, wherein the polyoxyalkylene polyol of the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component is selected from the group consisting of polyethylene ether glycol, polypropylene ether glycol, poly(tetramethylene ether) glycol, polyethers prepared by the copolymerization of cyclic ethers selected from the group consisting of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, and mixtures thereof, with aliphatic polyols selected from the group consisting of ethylene glycol,

1,3-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and mixtures thereof, and combinations thereof.

41. The multicomponent formulation of claim 37, wherein the polyoxyalkylene polyol of the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component is selected from the group consisting of polyethylene ether glycol, polypropylene ether glycol, poly(tetramethylene ether) glycol, polyethers prepared by the copolymerization of cyclic ethers selected from the group consisting of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, and mixtures thereof, with aliphatic polyols selected from the group consisting of ethylene glycol, 1,3-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, and mixtures thereof, and combinations thereof.

10 42. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate prepolymer component additionally comprises an allophanate.

15 43. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate prepolymer component additionally comprises a polyoxyalkylene polyol.

44. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate prepolymer component is isocyanate-terminated.

45. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate prepolymer component is hydroxy-terminated.

20 46. The multicomponent formulation of claim 37, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component has a number average molecular weight in the range of about 3,000 to about 20,000.

47. The multicomponent formulation of claim 37, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component has a number 25 average molecular weight in the range of about 6,000 to about 10,000.

48. The multicomponent formulation of claim 37, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component has a number average molecular weight in the range of about 1,000 to about 4,000.

49. The multicomponent formulation of claim 37, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component has a number average molecular weight in the range of about 1,500 to about 3,500.

50. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate component has a number average molecular weight in the range of about 250 to about 4,000.

51. The multicomponent formulation of claim 37, wherein the diphenylmethane diisocyanate component has a number average molecular weight in the range of about 250 to about 2,000.

10 52. The multicomponent formulation of claim 37, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component comprises about 10% to about 92% by weight of the reaction product.

15 53. The multicomponent formulation of claim 37, wherein the hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer component comprises about 20% to about 80% by weight of the reaction product.

54. The multicomponent formulation of claim 37, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component comprises about 1% to about 40% by weight of the reaction product.

20 55. The multicomponent formulation of claim 37, wherein the isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator component comprises about 5% to about 20% by weight of the reaction product.

56. The multicomponent formulation of claim 37, wherein the reaction product has a 100% modulus of about 40 psi to about 90 psi.

25 57. The multicomponent formulation of claim 37, wherein the mole ratio of isocyanate-terminated end groups to hydroxy-terminated end groups is about 0.5:1 to about 3:1.

58. The multicomponent formulation of claim 37, further comprising at least one component selected from the group consisting of UV absorbers, antioxidants,

stabilizers, mildewcides, biocides, fungicides, fire or flame retardants, fillers, pigments, adhesion promoters, flow and leveling additives, wetting agents, antifoaming agents, rheology modifiers, and mixtures thereof.

59. The multicomponent formulation of claim 37, further comprising at least one
5 UV stabilizer selected from the group consisting of 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, esters of substituted and unsubstituted benzoic acids, acrylates, nickel compounds, sterically hindered amines, oxanilides, 2-(2-hydroxyphenyl)-1,3,5-triazines, and mixtures thereof.

60. The multicomponent formulation of claim 37, further comprising at least one
10 antioxidant selected from the group consisting of alkylated monophenols, alkylthiomethylphenols, hydroquinones and alkylated hydroquinones, tocopherols, hydroxylated thiadiphenyl ethers, alkylidenebisphenols, O-, N- and S-benzyl compounds, hydroxybenzylated malonates, aromatic hydroxybenzyl compounds, triazine compounds, benzylphosphonates, acylaminophenols, esters of beta-(3,5-di-
15 tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, esters of beta-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, amides of beta-(3,5-di-tert-butyl-4-
20 hydroxyphenyl)propionic acid, ascorbic acid and derivatives, aminic antioxidants, and mixtures thereof.

61. The multicomponent formulation of claim 37, further comprising at least one
fire or flame retardant selected from the group consisting of triphenyl phosphate, polyammonium phosphate, monoammonium phosphate, tri(2-chloroethyl) phosphate,
25 melamine, exfoliated graphite, acid treated natural graphite flakes, and mixtures thereof.

62. The multicomponent formulation of claim 37, further comprising at least one
filler selected from the group consisting of carbon black, titanium dioxide, zinc oxide, glass spheres, iron particles, quartz, hydrophilic silica, hydrophobic amorphous fumed
30 silica, amorphous precipitated silica, barytes, limestone, sulfates, alumina, clays, diatomaceous earth, wollastonite, mica, perlite, flint powder, kryolite, talc, polymer

granules, polymer powders, micronized polymers, melamine, zinc oxide, and mixtures thereof.

63. The polyurethane sealant of claim 37, further comprising at least one pigment selected from the group consisting of carbon black, titanium dioxide, barium sulfate, zinc oxide, zinc sulfide, basic lead carbonate, antimony trioxide, lithopones, iron oxides, graphite, luminescent pigments, zinc yellow, zinc green, ultramarine, manganese black, antimony black, manganese violet, Paris blue, Schweinfurter green, sepia, gamboge, Cassel brown, toluidine red, para red, Hansa yellow, indigo, azo dyes, anthraquinonoid and indigoid dyes, dioxazine, quinacridone, phthalocyanine, 10 isoindolinone, and metal complex pigments, and mixtures thereof.

64. The multicomponent formulation of claim 37, further comprising at least one flow and leveling additive, wetting agent, or antifoaming agent selected from the group consisting of silicones, modified silicones, hydrocarbons, polyacrylates, fluorosurfactants, and mixtures thereof.

15 65. The multicomponent formulation of claim 37, further comprising at least one rheology modifier selected from the group consisting of fumed silica, hydroxyethyl cellulose, hydroxypropyl cellulose, and mixtures thereof.

66. The polyurethane sealant of claim 37, further comprising at least one adhesion promoter selected from the group consisting of

20 2-aminoethyl-dimethylmethoxysilane; 6-aminohexyl-tributoxysilane;
3-aminopropyl-trimethoxysilane; 3-aminopropyl-triethoxysilane;
3-aminopropyl-methyldiethoxysilane; 5-aminopentyl-trimethoxysilane;
5-aminopentyl-triethoxysilane and 3-aminopropyl-triisopropoxysilane,
 γ -glycidoxypolytrimethoxysilane, γ -glycidoxypolytriethoxysilane,
25 γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, and,
 γ -ureidopropyltrimethoxysilane, and γ -ureidopropyltriethoxysilane.

30 67. The polyurethane sealant of claim 37, wherein at least one component additionally comprises at least one chain extender selected from the group consisting of hydroxyl containing chain extenders and amine containing chain extenders.

68. The polyurethane sealant of claim 67, wherein said chain extender is selected from the group consisting of ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, neopentyl glycol, diethylene glycol, ethylene diamine, 1,3-propanediamine, 1,4-butanediamine, 1,3-pentanediamine, 1,5-pentanediamine, 5 1,6-hexamethylene diamine, 2-methylpentamethylenediamine, and mixtures thereof.

69. A method for making a sealant comprising:

- a) providing a base component, an activator component, and a modifier component, wherein the base component comprises a hydroxy-terminated toluenediisocyanate/polyoxyalkylene polyol prepolymer, the activator component comprises an isocyanate-terminated toluenediisocyanate/polyoxyalkylene polyol activator, and the modifier component comprises at least one of a diphenylmethane diisocyanate prepolymer and a diphenylmethane diisocyanate monomer; and
- b) combining the base component, activator component, and modifier component to form a polyurethane reaction product; wherein the reaction product is paintable in the absence of a primer and has a 100% modulus of less than about 100 psi in the absence of a plasticizer, and 15 wherein diphenylmethane diisocyanate (calculated as monomer) is about 1% to 3% by weight of said reaction product.

70. The method of claim 69, wherein the reaction product has a 100% modulus of about 40 psi to about 90 psi.

71. The method of claim 69, including combining the modifier component with 25 the activator component prior to combination with the base component.

72. The method of claim 69, including combining the modifier component with the base component prior to combination with the activator component.

73. The method of claim 69, further comprising applying the reaction product to a substrate.

74. The method of claim 73, wherein said applying is selected from the group consisting of spraying, brushing, rolling, and combinations thereof.

75. The method of claim 73, wherein the substrate is selected from the group consisting of concrete, stone, metal, glass, plastic, wood, and composite materials.

5 76. The method of claim 69, further comprising applying paint to the sealant.

77. The method of claim 76, wherein the paint is selected from the group consisting of latex paint, solvent-borne paint, and solvent-free paint.

78. The method of claim 76, wherein the paint adheres to the surface of the sealant with a rating of at least 4B when tested according to the paint adhesion test ASTM

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